σ-Bonded Organotransition Metal Ions. Part XV.[1] Preparation and Fluorine-19 Nuclear Magnetic Resonance Spectra of Some Monomeric Anionic, Cyanide-bridged Dimeric Anionic, and Related Fluorobenzylcobalt(III) Complexes

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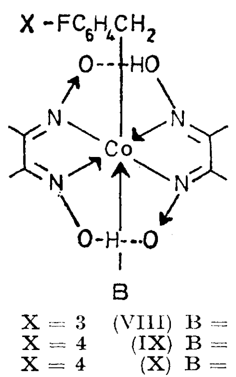
Fluorobenzylcobalt(III) complexes of the type (i) $4\text{-FC}_6H_4CH_2Co(dmgH)_2B^-$, where dmgH is the conjugate base of dimethylglyoxime and B = CN, N_3, NCO, Cl, Br, I, NO_2, NCS; (ii) $4\text{-FC}_6H_4CH_2Co(dmgH)_2CNCo(dmgH)_2R^-$, where R = Me, $CH_2C_6H_4F$, $CH_2C_6H_4NO_2$; (iii) $RCo(dmgH)_2CNCo(dmgH)_2CH_2C_6H_4F^-$, where R = Me, $CH_2C_6H_4NO_2$, C≡CPh; (iv) $4\text{-FC}_6H_4CH_2Co(dmgH)(dmgH_2)B$, where B = $CNCo(dmgH)_2CH_2C_6H_4F$, $CNCo(dmgH)_2CH_2C_6H_4NO_2$, CF_3CO_2; (v) $4\text{-FC}_6H_4CH_2Co(dotnH)B$, where dotnH is the conjugate base of 4,8-diaza-3,9-dimethylundeca-3,8-diene-2,10-dione dioxime and B = CF_3CO_2, CN; (vi) $4\text{-FC}_6H_4CH_2Co(dotnH)B^+$, where B = aq, py, Ph_3P; have been prepared and isolated and/or characterised in solution. The fluorine-19 spectra have been measured and the substituent chemical shifts relative to that of fluorobenzene have been related to the electron-donating capacity of the substituent CH_2Co(ligands). The electron-donating capacity of substituents of type (i) depend markedly upon the nature of the anionic ligand B, cyanide ion being particularly effective in promoting this electron donation. Cyanide ion is also very effective in the bridged cyanide complexes of types (ii) and (iii). Protonation of one of the dioximato-ligands of complexes of types (i), (ii), and (iii), or replacement of the two dioximato-ligands by the tetradentate ligand dotnH, more than outweighs the electron-donating influence of the monomeric or bridged cyanide ligand.

In a previous paper[2] we described fluorine-19 spectral studies of a number of organometallic compounds of the type 3- or $4\text{-FC}_6H_4CH_2ML_mL_n'$, where M is a transition metal and L_m and L_n' are combinations of mono- and poly-dentate ligands. The substituent chemical shift (s.c.s.) of the *para*-fluorine relative to that of fluorobenzene was used as an indication of the electron-donating capacity of the substituent $CH_2ML_mL_n'$ relative to that of hydrogen. Thus, where the chemical shift of the *para*-fluorine is more positive than that of fluorobenzene, the substituent is believed to be more electron donating than hydrogen towards the fluorophenyl group.[3] Several carbonyl-containing substituents, such as $CH_2Mn(CO)_4PPh_3$ and $CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$, were shown to be much more electron donating even than the methyl group towards the fluorophenyl group in the ground state, but the neutral groups of the type $CH_2Co(dmgH)_2B$, where dmgH is the conjugate base of dimethylgyoxime and B is a neutral ligand, were shown to be comparable with the methyl group and relatively insensitive to the nature of the ligand B. However, in the one case studied in which the ligand B was negatively charged (*i.e.*, B = CN^-), the electron-donating power of the substituent was markedly increased as shown by the surprisingly high substituent chemical shift for the ion $4\text{-FC}_6H_4CH_2Co(dmgH)_2CN^-$.

In this paper are described fluorine-19 n.m.r. studies of a variety of anionic, neutral, and cationic, complexes of cobalt in order to determine the influence of charge and the character of charged ligands on the substituent effect of metallomethyl groups.



(I) B = CN^-, X = 3
(II) B = CN^-, X = 4
(III) B = N_3^-, X = 4
(IV) B = NCS^-, X = 4
(V) B = SCN^-, X = 4
(VI) B = NCO^-, X = 4
(VII) B = NO_2, X = 4
(VIII) B = I^-, X = 4
(IX) B = Br^-, X = 4
(X) B = Cl^-, X = 4
(XI) B = $OCOCF_3^-$, X = 4
(XII) B = aq., X = 4
(XIII) B = NCMe, X = 4
(XIV) B = dmf, X = 4

RESULTS

(a) A series of monomeric anionic fluorobenzylbis(dimethylglyoximato)cobaltate(III) complexes (I—III, VI—X, and a mixture of IV and V) were prepared by addition of a salt of the corresponding anionic ligand B to the neutral 3-

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[1] Part XIV, D. Dodd and M. D. Johnson, *J.C.S. Dalton*, 1973, 1218.

[2] C. W. Fong and M. D. Johnson, *J.C.S. Perkin II*, 1973, 986.

[3] S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 9113 and refs. cited therein.

TABLE 1

Characteristics of organocobalt(III) complexes

Compound	Analysis Calc. (Found)			Infrared[a] cm⁻¹	¹H N.m.r.[b] (τ)		
	C	H	N		CH_2	dmgH	Other
$4\text{-}FC_6H_4CH_2Co(dmgH)_2CN^-\ Ph_4As^+$	59·5(58·8)	5·0(4·9)	8·7(8·8)	ν(CN) 2114			
$4\text{-}FC_6H_4CH_2Co(dmgH)_2CN^-\ Et_4N^+,H_2O$	50·4(49·8)	7·3(7·4)	14·7(15·1)	ν(CN) 2111	7·43[c]	8·02[c]	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2N_3^-\ Ph_4As^+$	56·9(56·4)	4·9(4·9)	11·9(11·9)		7·46	8·01	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2N_3^-\ Et_4N^+$	48·4(48·2)	7·0(7·0)	19·7(19·8)	ν(N_3) 2028	7·42	7·97	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2(NCS)^-\ Ph_4As^+$	57·2(57·4)	4·8(4·8)	8·3(8·3)		7·56, 7·21[d]	8·07, 7·98[d]	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2(NCS)^-\ Et_4N^+,H_2O$	47·7(47·3)	7·0(7·0)	13·9(14·0)	ν(CN) 2094,[e] 2115			
$4\text{-}FC_6H_4CH_2Co(dmgH)_2NCO^-\ Ph_4As^+,1/2CH_2Cl_2,$[f] $1/4Et_2O$[f]	56·3(55·7)	4·9(4·9)	7·9(7·8)		7·62	8·06	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2NO_2^-\ Ph_4As^+,3/4CH_2Cl_2,$[f] $1/4Et_2O$[f]	53·8(53·4)	4·9(4·8)	7·7(7·7)		7·58	8·06	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2Cl^-\ Ph_4As^+,2/3CH_2Cl_2,$[f] $1/6Et_2O$[f]	54·7(54·2)	4·9(4·7)	6·3(6·3)		7·50	8·04	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2Br^-\ Ph_4As^+,3/4CH_2Cl_2$[f]	51·6(51·9)	4·5(4·7)	6·1(6·4)		7·51	8·04	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2I^-\ Ph_4As^+,1/2CH_2Cl_2,$[f] $1/4Et_2O$[f]	50·2(49·5)	4·5(4·4)	5·8(5·3)		7·49	8·05	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2I^-\ Pr_4P^+$	44·5(44·2)	6·6(6·6)	7·7(7·0)		obscured	7·99	
$4\text{-}NO_2C_6H_4CH_2Co(dmgH)_2CN^-\ Et_4N^+,2H_2O$	46·7(46·7)	6·5(6·4)	15·9(16·4)	ν(CN) 2116	7·58	7·99	
$4\text{-}FC_6H_4CH_2Co(dmgH)(dmgH_2)CNCo(dmgH)_2CH_2C_6H_4F$	45·2(44·4)	5·0(5·0)	15·3(15·2)	ν(CN) 2146	7·19, 7·22	7·95, 7·99	−2·95[g]
$4\text{-}FC_6H_4CH_2Co(dmgH)(dmgH_2)OCOCF_3$	46·1(46·0)	4·6(4·9)	10·7(9·7)				
$4\text{-}FC_6H_4CH_2Co(dotnH)OCOCF_3,H_2O$	38·9(38·9)	4·3(4·5)	10·6(10·9)				
$4\text{-}FC_6H_4CH_2Co(dotnH)CN$	52·7(52·6)	5·8(6·2)	16·2(16·2)	ν(CN) 2118			
$4\text{-}FC_6H_4CH_2Co(dotnH)aq^+\ ClO_4,H_2O$	39·8(39·0)	4·6(5·0)	10·3(10·6)				
$4\text{-}FC_6H_4CH_2Co(dotnH)py^+\ ClO_4^-$	47·1(46·8)	4·8(5·1)	12·0(12·0)				
$4\text{-}FC_6H_4CH_2Co(dotnH)PPh_3^+\ ClO_4^-$	56·2(55·7)	5·0(4·9)	7·3(7·4)				
$3\text{-}FC_6H_4CH_2Co(dmgH)_2CN^-\ Et_4N^+,2H_2O$	48·8(49·2)	7·2(6·8)	14·2(13·1)	ν(CN) 2114	7·56	8·00	
$4\text{-}FC_6H_4CH_2Co(dmgH)_2CNCo(dmgH)_2Me^-\ Et_4N^+$				ν(CN) 2144			
$4\text{-}FC_6H_4CH_2Co(dmgH)_2CNCo(dmgH)_2CH_2C_6H_4F^-\ Et_4N^+$				ν(CN) 2146			
$4\text{-}FC_6H_4CH_2Co(dmgH)_2NCCo(dmgH)_2CH_2C_6H_4NO_2^-\ Et_4N^+$				ν(CN) 2148			
$4\text{-}FC_6H_4CH_2Co(dmgH)_2NCCo(dmgH)_2C{\equiv}CPh^-\ Ph_4As^+$				ν(CN) 2168 ν(C≡C) 2120			

[a] In $CHCl_3$. [b] In $CDCl_3$. [c] + 5% [²H]₄Methanol. [d] Ratio *ca.* 2 : 1. [e] Shoulder. [f] Based on ¹H n.m.r., not on analysis. [g] O–H · · · O.

or 4-fluorobenzylbis(dimethylglyoximato)aquocobalt(III) complex in aqueous solution or in methylene chloride solution. The corresponding salts, isolated directly or following the addition of an appropriate cation, are described in Table 1.

(b) A series of bridged anionic cyanide complexes (XV—XXII) were prepared by the addition of one equivalent of the appropriate organobis(dimethylglyoximato)aquocobalt(III) complex to a solution of the appropriate organobis(dimethylglyoximato)cyanocobaltate(III) salt in methylene chloride [equation (1)].[1] These bridged complexes were not isolated but were identified from their characteristic ¹H n.m.r. spectra and C≡N stretch at *ca.* 35 cm⁻¹ higher frequency than for the monomeric cyano-complexes.[1]

$$[RCo(dmgH)_2CN]^- + R'Co(dmgH)_2aq \rightleftharpoons [RCo(dmgH)_2CNCo(dmgH)_2R']^- + H_2O \quad (1)$$

(XV) $R = 4\text{-}FC_6H_4CH_2,\ R' = Me$;
(XVI) $R = Me,\ R' = 4\text{-}FC_6H_4CH_2$;
(XVII) $R = R' = 4\text{-}FC_6H_4CH_2$;
(XVIII) $R = 4\text{-}FC_6H_4CH_2,\ R' = 4\text{-}NO_2C_6H_4CH_2$;
(XIX) $R = 4\text{-}NO_2C_6H_4CH_2,\ R' = 4\text{-}FC_6H_4CH_2$;
(XX) $R = PhC{\equiv}C,\ R' = 4\text{-}FC_6H_4CH_2$;

possible that the former may be a bridged neutral complex analogous to (XXVI) below.

$$[4\text{-}FC_6H_4CH_2Co(dmgH)_2I]^- + H_3O^+ \rightleftharpoons \underset{\text{(XXIII)}}{4\text{-}FC_6H_4CH_2Co(dmgH)(dmgH_2)I} \quad (2)$$

$$4\text{-}FC_6H_4CH_2Co(dmgH)_2aq + CF_3CO_2H \rightleftharpoons \underset{\text{(XXIV)}}{4\text{-}FC_6H_4CH_2Co(dmgH)(dmgH_2)OCOCF_3} \quad (3)$$

(d) Two neutral dimeric bridged cyano-complexes (XXVI and XXVII) were prepared[4] by the addition of mineral acid to aqueous solutions of the monomeric anionic cyano-complex (II) in an attempt to prepare the neutral complex (XXV) [equations (4—8); $R = R' = 4\text{-}FC_6H_4CH_2$], and by the addition of mineral acid to an aqueous solution of the bridged anionic complex (XVIII) [equation (8); $R = 4\text{-}FC_6H_4CH_2$; $R' = 4\text{-}NO_2C_6H_4CH_2$], respectively.

$$[RCo(dmgH)_2CN]^- + H_3O^+ \overset{H_2O}{\rightleftharpoons} \underset{\text{(XXV) } R = 4\text{-}FC_6H_4CH_2}{RCo(dmgH)(dmgH_2)CN} \quad (4)$$

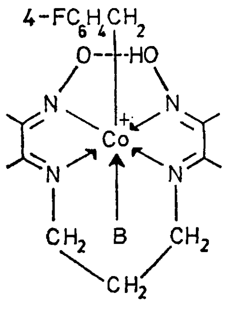
TABLE 2

Fluorine-19 substituent chemical shifts (s.c.s.) relative to fluorobenzene in methylene chloride

Formula	Compound	s.c.s./p.p.m.	
		CH$_2$Cl$_2$	Other
(II)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$CN$^-$ Na$^+$		5·42 (water)
(II)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$CN$^-$ Ph$_4$As$^+$	8·49	8·65 (dmf)
(II)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$CN$^-$ Et$_4$N$^+$	8·08	8·50(dmf) 5·35(water)
(VII)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$NO$_2$$^-$ Ph$_4$As$^+$	7·80	
(III)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$N$_3$$^-$ Et$_4$N$^+$	7·12	7·60(dmf) 4·09(water)
(III)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$N$_3$$^-$ Ph$_4$As$^+$	7·60	
(VI)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$NCO$^-$ Ph$_4$As$^+$	7·50	
(X)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$Cl$^-$ Ph$_4$As$^+$	7·04	
(IX)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$Br$^-$ Ph$_4$As$^+$	6·72	
(V or IV)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$(NCS)$^-$ Ph$_4$As$^+$	6·78	
(V or IV)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$(NCS)$^-$ Et$_4$N$^+$	6·38	6·59(dmf) 5·34, 5·36(water)
(VIII)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$I$^-$ Ph$_4$As$^+$	6·52	
(VIII)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$I$^-$ Pr$_4$P$^+$	6·17	
Bridged anionic complexes			
(XV)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$CNCo(dmgH)$_2$Me$^-$ Et$_4$N$^+$	7·69	
(XVIII)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$CNCo(dmgH)$_2$CH$_2$C$_6$H$_4$NO$_2$$^-$ Et$_4$N$^+$	7·68	
(XVIII)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$CNCo(dmgH)$_2$CH$_2$C$_6$H$_4$NO$_2$$^-$ Ph$_4$As$^+$	8·00	
(XVII)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$CNCo(dmgH)$_2$CH$_2$C$_6$H$_4$F$^-$ Et$_4$N$^+$	7·64(*C*-end) 6·57(*N*-end)	
(XVI)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$NCCo(dmgH)$_2$Me$^-$ Et$_4$N$^+$	6·65	
(XIX)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$NCCo(dmgH)$_2$CH$_2$C$_6$H$_4$NO$_2$$^-$ Et$_4$N$^+$	6·49	
(XX)	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$NCCo(dmgH)$_2$C≡CPh$^-$ Ph$_4$As$^+$	6·49	
Neutral complexes			
(XXVII)	4-FC$_6$H$_4$CH$_2$Co(dmgH)(dmgH$_2$)CNCo(dmgH)$_2$CH$_2$C$_6$H$_4$NO$_2$	4·29	
(XXVI)	4-FC$_6$H$_4$CH$_2$Co(dmgH)(dmgH$_2$)CNCo(dmgH)$_2$CH$_2$C$_6$H$_4$F	5·35(*N*-end) [a] 4·21(*C*-end) [a]	
(XXIV)	4-FC$_6$H$_4$CH$_2$Co(dmgH)(dmgH$_2$)OCOCF$_3$	2·37	5·35(dmf) 3·42(acetone) [b]
(XXIII)	4-FC$_6$H$_4$CH$_2$Co(dmgH)(dmgH$_2$)I	2·90 [c]	
(XXXII)	4-FC$_6$H$_4$CH$_2$Co(dotnH)OCOCF$_3$	2·88 [d]	4·49(dmf) 4·46(acetone) [e]
(XXXI)	4-FC$_6$H$_4$CH$_2$Co(dotnH)CN	5·32	6·25(dmf)
Cationic complexes			
(XXVIII)	4-FC$_6$H$_4$CH$_2$Co(dotnH)aq$^+$ ClO$_4$$^-$	3·83	4·85(dmf) [f]
(XXIX)	4-FC$_6$H$_4$CH$_2$Co(dotnH)py$^+$ ClO$_4$$^-$	2·36	3·34(dmf)
(XX)	4-FC$_6$H$_4$CH$_2$Co(dotnH)PPh$_3$$^+$ ClO$_4$$^-$	1·45 [d]	3·18(dmf)
Other complexes			
	3-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$CN$^-$ Et$_4$N$^+$	4·12	
	3-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$py	2·91	
	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$NCMe	4·79	
	4-FC$_6$H$_4$CH$_2$Co(dmgH)$_2$dmf	4·98	5·44(dmf)
	4-FC$_6$H$_4$Me	5·58	5·48(dmf) 5·48(acetone)
	4-FC$_6$H$_4$OMe	11·50	11·50(dmf) 11·45(acetone)

[a] When prepared *in situ* s.c.s. = 5·26 and 4·10 p.p.m., trace H$_2$O present. [b] Other resonance s.c.s. = 0·08 also present. [c] Not characterised. [d] +5% Methanol. [e] Other resonance s.c.s. = 0·12 p.p.m. [f] Other resonance s.c.s. = 2·2 p.p.m. also evident.

(e) Three cationic complexes (XXVIII—XXX) were prepared by standard methods and isolated as the perchlorate salts.[5] The two neutral complexes (XXXI and XXXII) were prepared from the triphenylphosphine- and aquo-complexes (XXX and XXVIII) by addition of cyanide ion and trifluoroacetic acid, respectively, in appropriate solvents. The characteristics of the five complexes are shown in Table 1.



(XXVIII) B = aq.; (XXXI) B = CN$^-$;
(XXIX) B = py; (XXXII) B = OCOCF$_3$$^-$
(XXX) B = PPh$_3$;

Fluorine-19 *N.M.R. Spectra*.—All the monomeric and dimeric complexes described above were diamagnetic and gave one or two multiplet (AA′BB′X) fluorine resonances, respectively. In a few cases described below, more resonances were observed than had been expected. The values of the substituent chemical shifts observed in all cases and for several model compounds (*e.g.* XII—XIV) are shown in Table 2.

[5] G. Costa, G. Mestroni, and E. de Savorgnani, *Inorg. Chim. Acta*, 1969, **3**, 323.

DISCUSSION

(a) *Anionic Monomeric Complexes.*—The character of the monomeric cyanobis(dimethylglyoximato)cobaltate(III) complexes has been discussed in some detail.[1] Their salts are usually soluble in methylene chloride, in dimethylformamide, and in water, in which they are largely undissociated. As expected therefore, the ^{1}H n.m.r. of the 4-fluorobenzylbis(dimethylglyoximato)cyanocobaltate(III) salts in methylene chloride and in deuteriochloroform in each case show the presence of only a single species; single fluorine-19 multiplet resonances are also observed (Table 2). The cyanato- and azido-complexes are similar, but are much more prone to dissociation in solution, such that only in the deuteriochloroform and methylene chloride solutions are they largely undissociated.[1] The ^{1}H n.m.r. spectrum of the 4-fluorobenzylbis(dimethylglyoximato)-azido- and -cyanatocobaltate(III) complexes each show the presence of a single species in deuteriochloroform and a single fluorine-19 multiplet resonance is also observed in methylene chloride (Table 2). Organobis(dimethylglyoximato)-thiocyanatocobaltate(III) complexes on the other hand are known [1] to exist as mixtures of the *N*- and *S*-bonded species and the ^{1}H n.m.r. spectrum of 4-fluorobenzylbis-(dimethylglyoximato)thiocyanatocobaltate(III) complex in deuteriochloroform and in methylene chloride shows clearly the presence of the two isomers, believed to be the *N*- and *S*-bonded species (IV and V, respectively) in the ratio *ca.* 2 : 1. It is surprising therefore, that only a single clean fluorine-19 resonance multiplet is observed for this complex in methylene chloride. In view of the sequence described below, the most probable explanation, that the two resonances coincide, is unexpected. In aqueous solution the complex shows two broad overlapping fluorine-19 resonances which we ascribe to a moderately fast exchange, probably between the two monomeric complexes through either the bridged dimeric species [1] $[F\text{-}C_6H_4CH_2Co(dmgH)_2SCNCo(dmgH)_2CH_2C_6H_4F]^-$ or the dimeric complex $[FC_6H_4CH_2Co(dmgH)_2]_2$.[6]

Organobis(dimethylglyoximato)-nitrito- and -halogenocobaltate(III) salts have not previously been described. Though methylbis(dimethylglyoximato)nitritocobaltate(III) salts may be isolated from aqueous solutions of nitrite ion and the corresponding aquo-complex (XII), we were able only to isolate the 4-fluorobenzylbis(dimethylglyoximato)nitritocobaltate(III) ion as the tetraphenylarsonium salt from the reaction of the aquo-complex with tetraphenylarsonium nitrite in methylene chloride. Similar preparations of the halogeno-complexes were carried out because of the even greater lability of these complexes in aqueous solution. The ^{1}H n.m.r. spectra of these complexes in deuteriochloroform clearly indicated the presence of a single species in each case and single fluorine-19 multiplets were also observed.

The substituent chemical shifts of these anionic monomeric complexes show a number of interesting features. First, the substituent chemical shifts for the anionic complexes are all greater than those observed for the corresponding neutral complexes such as (XII—XIV). Secondly, the range of values observed for the anionic complexes is much larger than the range observed for the neutral cobaloxime complexes.[2] Thirdly, the values for all the anionic complexes are markedly dependent upon the nature of the solvent and of the counter-ion.

In methylene chloride solution, ion-pairing between the complex anion and the cation is to be expected, and the consistently higher substituent chemical shifts observed (+0·3—0·4 p.p.m.) for the tetraphenylarsonium salts than for the tetraethylammonium salts suggests that the ion-pairing is greater with the latter cation. In dimethylformamide, in which less ion-pairing and greater cation solvation are to be expected, the substituent chemical shifts are higher, but in water, in which solvation of the anionic complex would be expected to be appreciable, the substituent chemical shifts are much lower; comparable with those of the neutral cobaloxime complexes.

The order of effectiveness of the negatively charged ligands for a particular cation is: $CN^- > NO_2^-$ (*N*-bonded?) $> N_3^- > NCO^-$ (*N*-bonded) $> Cl^- > Br^- \sim NCS^-$ (*N*- and/or *S*-bonded) $> I^-$. Since all of the substituent chemical shifts caused by these anionic ligands are higher than those caused by neutral ligands, it is apparent that any simple correlation with spectrochemical series, basicity, *etc.*, must be ruled out, except within a particular series of neutral or anionic ligands. Indeed, if the very existence of a negative charge on the metal atom is sufficient to cause a large increase in the substituent chemical shift, then the variation of that shift with the character of the anionic ligand is probably a measure of the extent to which that ligand induces a negative charge on the metal. The above order is consistent with this suggestion, being approximately the order of proton basicity [7] of the ligands, but quite different from the order of association constants of the ligands towards bis(dimethylglyoximato)cobalt(III).[8] Very similar orders have been observed for the influence of *trans*-anionic ligands on the fluorine-19 resonances of 3-fluorophenylplatinum(II) complexes [9] and 3-fluorophenyl(4,8-diaza-3,9-dimethylundeca-3,8-diene-2,10-dione dioximato)cobalt(III) complexes,[10] though the spread of substituent chemical shifts and the numbers of ligands considered were much smaller.

The other question involves the influence of the negatively charged substituent on the fluorine-19 resonance and whether this effect is transmitted through the molecule or as a field effect. Comparison of the pair of compounds 3-fluorobenzylbis(dimethylglyoximato)-cyano- and -acetonitrile-cobalt(III) (s.c.s. 4·12 and 2·90 p.p.m., respectively) with the corresponding pair 4-fluorobenzylbis-(dimethylglyoximato)-cyano- and -acetonitrile-cobalt(III)

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[6] A. W. Herlinger and T. L. Brown, *J. Amer. Chem. Soc.*, 1972, **94**, 388.

[7] R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319.

[8] D. Dodd and M. D. Johnson, *J. Organometallic Chem.*, 1973, **52**, 1.

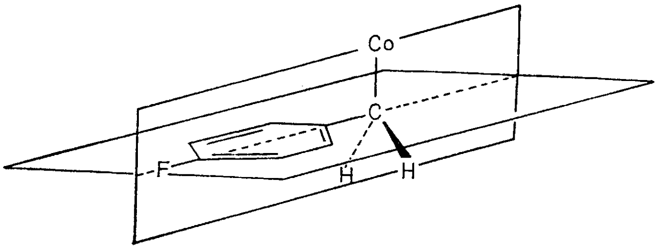
[9] G. W. Parshall, *J. Amer. Chem. Soc.*, 1966, **88**, 704.

[10] H. A. O. Hill, K. G. Moralee, F. Cernivez, and G. Pellizer, *J. Amer. Chem. Soc.*, 1972, **94**, 277.

(s.c.s. 8·08 and 4·79 p.p.m., respectively) shows that the increase in substituent chemical shift for the negatively charged substituent in the 4-position (3·29 p.p.m.) is substantially greater than that in the 3-position (1·22 p.p.m.). Even allowing for a vector influence of the field on the fluorine-19 resonance,[11] the enhanced effect in the 4-position is too great to be due solely to a field effect. Unfortunately, apart from a few studies using methanol and aqueous methanol,[12] detailed studies of the field effect on fluorine resonances have not been carried out, and there exist no suitable comparisons with our studies in methylene chloride solution. However, the change from 4-fluorotoluene to the 4-fluorophenylacetate ion (Δ s.c.s. 0·9 p.p.m.) in methanol is greater than that from 3-fluorotoluene to the 3-fluorophenylacetate ion (Δ s.c.s. —0·1 p.p.m.), being in the same direction as that observed here but of much smaller magnitude.

In the absence of a major field effect, the very large electron-donating influence of these negatively charged metallomethyl substituents is too great to be due entirely to an inductive effect. It is consistent with the corresponding large effects evident in the fluorine-19 resonances of fluorobenzene containing other metallomethyl substituents such as CH_2SnMe_3,[13] $CH_2Mn(CO)_4PPh_3$,[2] and $CH_2Fe(CO)_2(\pi\text{-}C_5H_5)$[2] and may be attributed to the hyperconjugative effect.[14] This effect, also termed σ,π-conjugation, is believed to involve overlap of metal–carbon bonding σ-orbitals with π-orbitals of the benzyl group, is necessarily directional, and would require the orientation shown in (XXXIII). However, the effectiveness of the same orientation has also been ascribed to a combination of *p*-*d*-homoconjugation and hyperconjugation.[15]

(b) *Dimeric Anionic Complexes.*—Bridged anionic cyano-complexes have also been examined in some detail.[1] They are characterised by a markedly higher frequency cyanide stretching vibration than is observed for the monomeric complexes, and by the presence of two sets of resonances in the ^1H n.m.r. spectrum due to the two different pairs of organic ligands and equatorial ligands. Those bridged complexes which have the same organic ligands and the same equatorial ligands, such as (XVII), are relatively stable in a variety of solvents, whereas those complexes which have two different organic ligands [such as (XV) and (XVIII)] are unstable and slowly rearrange to mixtures of bridged isomers.[1]



(XXXIII)

For example, the complex (XVII) shows two distinct sets of proton and fluorine-19 resonances, due to the dissimilar fluorobenzyl groups, which do not change with time. Similarly, fresh solutions of the unsymmetrical complexes (XV), (XVI), and (XVIII—XX), each show only a single set of fluorine-19 resonances, but these change over a period of *ca.* 24 h to mixtures of resonances of the four possible bridged isomers. Thus, the nitrobenzyl–fluorobenzyl complex (XIX) and the fluorobenzyl–nitrobenzyl complex (XVIII) each rearrange to a mixture containing (XVIII), (XIX), the fluorobenzyl–fluorobenzyl complex (XVII), and the nitrobenzyl–nitrobenzyl complex (XXII). The fluorine-19 resonances of these complexes overlap to such an extent that only two sets of multiplets can be distinguished in the final mixture.

The interesting features of the substituent chemical shifts of the individual anionic cyanide-bridged complexes are (i) the insensitivity of the higher field resonance (that of the fluorobenzylcobalt attached to the cyanide carbon) to the nature of the other terminal group; (ii) the relatively small effect of co-ordination of the second organocobalt to the monomeric cyano-complex on the fluorine resonance of the latter. Thus, the substituent chemical shift of the tetraethylammonium salt of the monomeric cyano-complex (II) changes from 8·08 to 7·66 ± 0·03 p.p.m. on co-ordination of the terminal nitrogen to methyl-, 4-nitrobenzyl-, or 4-fluorobenzyl-bis-(dimethylglyoximato)cobalt(III). Clearly, the electron-donating effect of the cyanocobaltate(III) group is little diminished on co-ordination of the cyanide nitrogen atom to neutral metallic species; *i.e.*, the extent of formal negative charge on the cobalt bonded to cyanide carbon is largely unaffected by such co-ordination. This confirms previous observations that ligand field strength of *C*-cyano-complexes is little influenced by bridging at the terminal nitrogen atom.[16]

It is surprising, therefore, to find (iii) that the substituent chemical shift (6·49—6·65 p.p.m.) of the 4-fluorobenzylcobalt, to which is co-ordinated the terminal nitrogen of an anionic cyanocobaltate(III) complex, is also appreciably larger than that observed when simple neutral nitrogen ligands are co-ordinated to the same fluorobenzylcobalt complex [*e.g.*, s.c.s. 4·79 p.p.m. for (XIII)]. Indeed, the substituent chemical shift of the *N*-bonded 4-fluorobenzylcobalt in these bridged complexes is comparable with that observed for the monomeric thiocyanato complex (IV or V) in methylene

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[11] M. J. S. Dewar and T. G. Squire, *J. Amer. Chem. Soc.*, 1968, **90**, 210; M. J. S. Dwear and Y. Takeuchi, *ibid.*, 1967, **89**, 390; W. Adcock and M. J. S. Dewar, *ibid.*, 1967, **89**, 379.

[12] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709 and 3146.

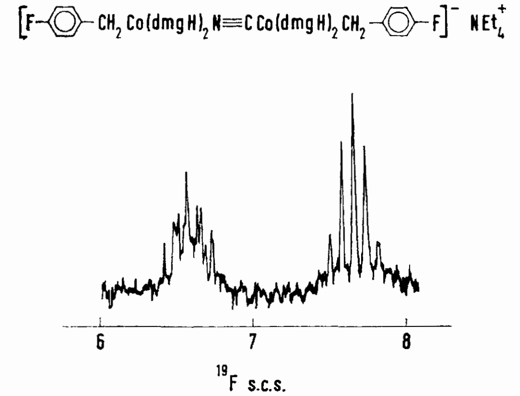
[13] A. J. Smith, W. Adcock, and W. Kitching, *J. Amer. Chem. Soc.*, 1970, **92**, 6140.

[14] R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 1964, 4804; W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, 1970, **92**, 829, 4476; J. H. Jerkunica and T. G. Traylor, *ibid.*, 1971, **93**, 6278; B. E. Cooper and W. J. Owen, *J. Organometallic Chem.*, 1971, **29**, 33; A. R. Lyons and M. C. R. Symons, *Chem. Comm.*, 1971, 1068.

[15] T. Kavamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 648; M. C. R. Symons, *ibid.*, p. 8589.

[16] R. A. de Castello, C. P. Mac-Coll, and A. Haim, *Inorg. Chem.*, 1971, **10**, 203.

chloride, in agreement with previous observations [17] that the ligand field strength of an *N*-bonded cobalt is comparable with that of the corresponding cyanato- and thiocyanato-complexes. It is apparent that the bridging cyanide ligand is appreciably electron donating in both directions, such that a structure of the type (XXXIV) would appear to contribute significantly to the character of the complex. (iv) In each of the appropriate bridged cyanide complexes, the fluorine resonance of the fluorobenzylcobalt co-ordinated to the cyanide carbon is a simple five-line multiplet, whereas that of the fluorobenzylcobalt attached to the cyanide nitrogen is more complex (see the Figure).



94·1 MHz Fluorine-19 magnetic resonance spectrum of an anionic cyanide-bridged complex, showing typical resolution under the conditions used. The higher field resonance is that of the *C*-bonded fluorobenzylcobalt

$$\mathrm{FC_6H_4CH_2}\overset{-}{\mathrm{(Co)}}\text{-}\overset{+}{\mathrm{C}}\mathrm{=N}\text{-}\overset{-}{\mathrm{(Co)}}\mathrm{CH_2C_6H_4F}$$

(XXXIV)

[where (Co) represents $Co(dmgH)_2$]

(c) *Neutral Bridged Complexes*.—Neutral bridged cyanide complexes of cobaloximes have not previously been reported, and their formation on protonation of the monomeric anionic complexes is surprising. Their proton resonance spectra show two distinct sets of resonances due to the two organic ligands and two sets of resonances due to the two sets of equatorial ligands, one of the latter sets carrying the extra proton. Protonation of one of the equatorial ligands of the anionic bridged complex (XVII) (s.c.s. 7·64 and 6·57 p.p.m.) causes a marked decrease in the substituent chemical shifts of both fluorine nuclei, to 4·21 and 5·33 p.p.m., respectively. Comparison with the changes of substituent chemical shift on protonation of the complex (XVIII) (s.c.s. 7·68 p.p.m.) to the neutral complex (XVII) (s.c.s. 4·29 p.p.m.) shows that it is the fluorobenzylcobalt attached to the cyanide carbon which is the more affected by this protonation [Δ s.c.s. 3·43 and 3·39 p.p.m. for (XVI) and (XXVII), respectively]. Thus, in the neutral bridged complex, the protonation of a dimethylglyoximato-ligand more than outweighs the influence of the anionic cyanide bridging ligand, such that the fluorine resonance of the fluorobenzylcobalt attached to the protonated dimethylglyoximato-ligand and to the cyanide carbon has a lower substituent chemical shift than is found in normal neutral fluorobenzylbis(dimethylglyoximato)cobalt(III) complexes.

(d) *Neutral Monomeric Complexes*.—The only well characterised neutral monomeric cobaloxime complex prepared was (XXIV), which shows the expected single proton resonance for the organic group and a singlet for the methyl protons of the protonated set of equatorial ligands. In methylene chloride solution the single fluorine-19 resonance has a substituent chemical shift of 2·37 p.p.m. which, on comparison with the results for the neutral dimeric complexes and the anionic monomeric complexes above, is about that expected for a complex which contains a protonated dimethylglyoximato-ligand and a weakly co-ordinating, weakly basic, anionic, axial ligand. The resonance at a substituent chemical shift of 2·88 p.p.m. observed in the acidic solutions of the iodo-complex (VIII) is similarly consistent with the neutral complex (XXIII). The trifluoroacetate complex (XXIV), which is also novel, was studied in two other solvents. In dimethylformamide, the observed substituent chemical shift (5·35 p.p.m.) suggests that the trifluoroacetic acid has been displaced and that it is the dimethylformamide complex (XIV) which is under observation. In acetone two resonances were observed; one at a substituent chemical shift of 3·42 p.p.m. and a second at 0·08 p.p.m. The former may be associated with the complex (XXIV), but the latter would be characteristic of a cationic complex such as that formed on replacement of the trifluoroacetate ion of (XXIV) by acetone. Conductivity measurements indicate that the neutral complex (XXIV) does have greater conductivity in acetone solution than would be expected for a neutral complex.

A similar neutral trifluoroacetate complex (XXXII), which has also been characterised, has a substituent chemical shift of 2·88 p.p.m., indicating that the dimethylglyoximato–dimethylglyoxime equatorial ligand group has a similar electronic effect to that of the tetradentate 4,8-diaza-3,9-dimethylundeca-3,8-diene-2,10-dione dioximate (dotnH) ligand. As expected the substituent chemical shift of the neutral cyano-complex (XXXI) is appreciably higher than that of the neutral trifluoroacetate complex (XXXII) in accord with the influence of cyanide and other ligands on the chemical shift of the complexes (II—X). Indeed, a comparison of the substituent chemical shift of complex (XXXI) (5·32 p.p.m.) with those of the neutral bridged complex (XXVII) (4·29 p.p.m.), the anionic bridged complex (XV) (7·69 p.p.m.), and the monomeric cyanide complex (II) (8·08 p.p.m.), confirms the view that the ligand pair dimethylglyoximato–dimethylglyoxime is comparable with the tetradentate ligand dotnH of similar total charge.

(e) *Cationic Complexes*.—The substituent chemical shifts of the cationic complexes (XXVIII—XXX) also appear to be susceptible to the nature of the axial base. This may be a result of the lower stability constants of these complexes allowing greater dissociation of the

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[17] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, 1965, **4**, 725.

neutral axial ligand in the non-polar solutions.[18] However, all the values are markedly lower than were observed for the neutral dimethylglyoximato- or dotnH complexes in accord with the expected influence of charge on the substituent effect of these groups.

EXPERIMENTAL

Materials.—3- And 4-fluorobenzylbis(dimethylglyoximato)aquocobalt(III),[2] 4-nitrobenzylbis(dimethylglyoximato)pyridinecobalt(III),[8] tetraethylammonium methylbis(dimethylglyoximato)cyanocobaltate(III),[1] and tetraphenylarsonium phenylethynylbis(dimethylglyoximato)cyanocobaltate(III) [1] were prepared as described previously. 4-Nitrobenzylbis(dimethylglyoximato)aquocobalt(III) was prepared by Mr. S. N. Anderson from 4-nitrobenzyl iodide by the method of Yamazaki and Hohokabe.[19]

Tetraphenylarsonium azide, thiocyanate, cyanate, nitrite, chloride, bromide, and iodide, were prepared by the addition of an excess of a saturated aqueous solution of the appropriate alkali metal salt to a saturated alkaline aqueous solution of tetraphenylarsonium chloride hydrochloride (Koch–Light). The white crystalline precipitate of the product was filtered off and dried *in vacuo* without further purification.

Tetraphenylarsonium and tetraethylammonium [2] *4-fluorobenzylbis(dimethylglyoximato)cyanocobaltate*(III), *tetraethylammonium 4-fluorobenzylbis(dimethylglyoximato)azidocobaltate*(III), *tetraethylammonium 4-fluorobenzylbis(dimethylglyoximato)thiocyanato-*(and *isothiocyanato-*)*cobaltate*(III), tetraethylammonium 3-fluorobenzylbis(dimethylglyoximato)cyanocobaltate(III) [2] were prepared from the respective aquo-complexes and aqueous solutions of the sodium salts of the appropriate anions in the manner described previously for the methyl complexes.[1]

by dissolution of the appropriate aquo-complex in a solution of one mole equivalent of the appropriate cyano-complex. Bridge formation was confirmed by the characteristically high ν(CN) in the i.r. spectrum measured in chloroform solution (Table 1) and from the ^{1}H n.m.r. spectra. The neutral bridged complex *cyano-*N*-4-fluorobenzylbis(dimethylglyoximato)cobalt*(III)*-*C*-4-fluorobenzyldimethylglyoximatodimethylglyoximecobalt*(III) was prepared from tetraethylammonium 4-fluorobenzylbis(dimethylglyoximato)cyanocobaltate(III). The latter (0·30 g) in water (5 ml) was treated with fluoroboric acid (42%, 5 drops), sufficient to complete precipitation of the yellow product. The yellow precipitate was filtered off, washed with water, and dried *in vacuo*. Yield 0·18 g (81%). The preparation and characterisation of a number of analogues of this compound will be described elsewhere.[4] The corresponding neutral bridged complex (XXVII) was prepared *in situ* in methylene chloride solution by addition of aqueous fluoroboric acid (42%) to a fresh solution of tetraphenylarsonium cyano-*N*-4-nitrobenzylbis(dimethylglyoximato)cobalt(III)-*C*-4-fluorobenzylbis(dimethylglyoximato)cobaltate(III). *4-Fluorobenzyldimethylglyoximatodimethylglyoximetrifluoroacetatocobalt*(III) was precipitated when 4-fluorobenzylbis(dimethylglyoximato)aquocobalt(III) was dissolved in trifluoroacetic acid and poured into water.

4-Fluorobenzyl(4,8-*diaza*-3,9-*dimethylundeca*-3,8-*diene*-2,10-*dionedioximato*)*-aquo-*, *-pyridine-*, and *-triphenylphosphine-cobalt*(III) *perchlorate* were prepared by the reaction between 4-fluorobenzyl chloride and the 4,8-diaza-3,9-dimethylundeca-3,8-diene-2,10-dionedioximatocobaltate(I) ion in methanolic solution. *4-Fluorobenzyl*(4,8-*diaza*-3,9-*dimethylundeca*-3,8-*diene*-2,10-*dione dioximato*)*cyanocobalt*(III) was prepared by addition of an excess of sodium cyanide